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TITLE: Resolution of Cyclic Bases by Means of Bromcyanogen (II)

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GI For diagram(s), see printed CA Issue.

AB cf. C. A., 2, 118. Piperidocyanamide and p-toluidine hydrochloride, at 160°, form the guanidine derivative, C₅H₁₀NC(:NH)NHC₆H₄Me; crystalline, m. 115°. Picrate, m. 132°. Chloroplatinate, m. and evolves gas 205°. Phenyl derivative, from PhNH₂; brittle crystalline mass. Picrate, m. about 107°. Chloroplatinate, orange-red, m. 195°. Dipiperido compound, C₅H₁₀NC(:NH)NC₅H₁₀, from piperidine hydrobromide and also from bromocyanogen and piperidine, without a solvent; colorless liquid with a slight basic odor, b₁₂ 175-7°. Picrate, well developed, yellow needles, m. 148°. Chloroplatinate, m. 192-200°, according to the rapidity of heating. γ-Phenoxypropylpiperidine, C₅H₁₀NCH₂CH₂CH₂OPh, is easily prepared from piperidine and iodopropyl phenyl ether. Hydriodide, m. 183°. Methiodide, m. 159-60°. Bromocyanogen reacts with it to form cyanopiperidine, bromopropyl phenyl ether, .vepsiln.-bromamyl-γ-phenoxypropylcyanamide and piperidocyanamide. The first of these, together with phenoxypropylpiperidine, its hydrobromide and bromcyanogen are extracted by means of dilute acid, the other 3 are dissolved out by Et₂O. The residue, after distillation of the Et₂O, was subjected to the reactions described below. (I) When heated with fuming HBr, at 105-7°, piperidine hydrobromide, trimethylene bromide and .vepsiln.-bromoamyl-γ-bromopropylcyanamide, BrCH₂(CH₂)₃CH₂N(CN)CH₂CH₂CH₂Br, are produced. Colorless oil which could not be distilled. Yield, about 50%. (2) Sodium phenolate forms piperidine cyanide, trimethyleneglycoldiphenyl ether (PhOCH₂CH₂)₂CH₂, and the cyanamide, PhOCH₂(CH₂)₃CH₂N(CN)CH₂CH₂CH₂OPh, which are separated by fractional distillation. Crystalline, m. 36°; b₁₀ 100-30°. Yield, about 60%. (3) Condensation with piperidine leads to the formation of piperidocyanamide, phenoxypropylpiperidine, and piperidylcyanophenoxypropylpentamethylenediamine. The second of these, PhOCH₂CH₂CH₂NC₅H₁₀, is a pale yellow liquid with a basic odor. Its salts are oily. Picrate, chloraurate, chloroplatinate. Methiodide, plates. With HBr it gives the compound BrCH₂CH₂CH₂NHC₅H₁₀. Salts oily. Yield of the phenoxy compound 50%. (4) Methylaniline forms cyan piperidine, methylphenylcyanamide. Methylphenylcyanophenoxypropylpentamethylenediamine, PhNMeCH₂(CH₂)₃CH₂N(CN)CH₂CH₂CH₂OPh, and phenoxypropylmethylaniline, PhOCH₂CH₂CH₂NMePh; oil, b₁₀ 217°. Picrate, yellow plates, m. 111°. The diamine is a viscid, yellowish red, odorless liquid, b₁₀ 300-25°. Its salts crystallize with difficulty. (5) Aniline gives sym. diphenylguanidine, phenylcyanophenoxypropylpentamethylenediamine, PhNHCH₂(CH₂)₃CH₂NMeCH₂CH₂CH₂OPh, and phenoxypropylaniline. Hydrochloride, crystalline, m. 165°. Benzoyl derivative, m. 120°. The diamine mentioned above is a viscid, yellowish red liquid, b₁₀ 300-20°. All its derivatives are oily. (6) Potassium cyanide gives γ-phenoxybutyric nitrile and phenoxy .vepsiln.-leucine nitrile, NCCH₂(CH₂)₃CH₂N(CN)CH₂CH₂CH₂NOPh; oil, b₁₅ 230-60°. When hydrolyzed it yields the acid, PhOCH₂CH₂CH₂N(CN)CH₂(CH₂)₃CH₂CO₂H; colorless, m. 131°. (7) Potassium phthalimide reacts readily, but

the products could not be separated. N-Propylpiperidine and bromocyanogen form piperidinecyanamide, propyl bromide, .vepsiln.-bromamylpropylcyanamide and piperidylcyanopropylpentamethylenediamine, $C_5H_{10}NCH_2(CH_2)_3CH_2N(CN)C_3H_7$; yellow, viscid liquid with a slightly basic odor, b₉ 196°. Picrate and methiodide, oily. It is hydrolyzed to the diamine, $C_5H_{10}NCH_2(CH_2)_3CH_2NHC_3H_7$; water-clear, mobile liquid, b₁₂ 146-50°. Picrate, lustrous crystals, m. 175°. Chloroplatinate, orange-red, m. and decomposes 228°. Methiodide, benzenesulphonyl and benzoyl derivatives, oily. Ethyl β -piperidopropionate, $C_5H_{10}NCH_2CH_2CO_2Et$, b. 230°, not 218° as stated by Wedekind. Picrate, long, yellow crystals, m. 127°. Methiodide, oily. With bromocyanogen the chief product is the original ester hydrobromide (43%); apparently some ethyl acrylate is also formed. The remaining material was condensed with piperidine; the products of the reaction which were identified were dipiperidylguanidine, cyanopiperidine and piperidocyanamide. γ -Phthalimidopropylpiperidine, formula (I) below, is a colorless, crystalline powder, m. 50°. Picrate, m. 190°. With bromocyanogen there are formed piperidocyanamide, γ -bromopropylphthalimide, and a bromo derivative, probably (II); pale yellow, very viscid oil. N-Ethylpiperidine and bromocyanogen form N-ethylpiperidine hydrobromide, cyanopiperidine, EtBr and .vepsiln.-bromethylcyanamide. This last was separated by condensation with piperidine to piperidylcyanethylpentamethylenediamine, $C_5H_{10}NCH_2(CH_2)_3CH_2NEtCN$; viscid, slightly colored liquid, b₁₁ 191-2°. Yield, about 50% of the ethylpiperidine. Picrate, oil. At 140°, with HCl, 70% of the base is hydrolyzed to piperidylethylpentamethylenediamine, $C_5H_{10}NCH_2(CH_2)_3CH_2NHEt$; colorless liquid, b₁₀ 132°. Picrate, reddish yellow crystals, m. 151°. Chloroplatinate, orange-red, crystalline powder, m. 220°. Diethyl sodiomalonate and (II) condense to form a mixture of substances, which could not be distilled. When hydrolyzed with HCl, or HBr, at 180°, there are formed butyric acid, piperidine and ζ -ethylaminoheptylic acid, $EtNHCH_2(CH_2)_4CH_2CO_2H$; colorless solid, m. 129-30°. Benzenesulphonyl derivative, oily. Chloroplatinate, m. 117°. The acid easily becomes yellow when heated and passes into an anhydride. By the interaction of piperidoacetonitrile and bromocyanogen the ratio of formation of cyanopiperidine to the pentamethylene derivative is about 3:1, in the case of ethylpiperidine it is 2:1 and with propylpiperidine 2:3.

IT 32599-03-4, Piperidine, 1-(γ -phenoxypropyl)-
(derivs.)

RN 32599-03-4 CAPLUS

CN Piperidine, 1-(3-phenoxypropyl)- (7CI, 8CI, 9CI) (CA INDEX NAME)

